Antiferromagnetism of S=1/2 Triangles in La4Cu3MoO12 (SOLID STATE CHEMISTRY-Multicomponent Materials)

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Masaki Azuma, Shintaro Ishiwata and Mikio Takano

Magnetic properties of a cupric triangular cluster compound $La_4Cu_3MoO_{12}$ were investigated. Susceptibility data show that paramagnetic cupric spin (S=1/2) above room temperature form S=1/2 trimers at lower temperatures because of strong intra-trimer antiferromagnetic interactions. The cluster moments acquire antiferromagnetic order below 2.6 K. The trimers can be polarized in an external field of 20 T at 1.3 K. The magnetization remains nearly constant at 1 μ_B per trimer up to a magnetization plateau at 55 T.

Keywords: Spin trimer/ Magnetic susceptibility/ High field magnetization/ Neutron scattering

The spin quantum number (small, large, integer, half-integer) and the geometry of the magnetic sublattice affect the ground state of quantum antiferromagnets in various fashions. For examples, spin singlet ground states with finite gaps to magnetic excited states have been found in several 1D antiferromagnetic (AF) systems such as S=1/2 alternating bond chains, S=1/2 2-leg ladders and S=1 chains (Haldane systems). The discovery of inorganic model compounds such as $CuGeO_3$ (spin-Peierls), $(VO)_2P_2O_7$ (alternating chain) [1], Y_2BaNiO_5 (Haldane), $SrCu_2O_3$ [2] and $Sr_{14}Cu_{24}O_{41}$ (ladders) in the past decade has stimulated keen interest in such 1D systems. Their large AF interactions (J) and the thermal stability make it rather easy to finely tune the electronic properties of these materials by means of chemical doping.

In the gapped ground states of these compounds, two neighboring S=1/2 spins form a spin singlet. On the other hand, AF trimer compounds are rare in nature. $La_4Cu_3MoO_{12}$ is a layered compound with an average structure of the $YAlO_3$ type [3]. The Cu_3MoO_4 layer of this compound shown in Fig. 1 can be derived from a triangular CuO layer by replacing a quarter of the Cu^{2+} ions with nonmagnetic Mo^{6+} ions. One can consider the Cu_3MoO_4 layer as being made of Cu_3O triangular clusters as suggested from the bond lengths : The average Cu-O bond lengths within the triangle, 1.983Å, is much shorter than that between neighboring triangles of 2.690Å. The Cu_3MoO_4 layers are separated from each other by /O/La/O/ layers. The structure can be described as a quasi-2D orthorhombic lattice made of slightly distorted cupric (S=1/2) trimers [4].

Figure 2 shows the temperature dependences of magnetic susceptibility and its inverse measured on heating from 5 to 800 K in an external field of 1 T. The susceptibility above 400 K was fitted well to the Curie-Weiss law with μ_{eff} = 1.81 (g = 2.09) and a Weiss temperature (θ) of -558 K. On the other hand, the slope of the $1/\chi$-T plot below 250 K decreased to 0.39 times the high-temperature value. The small Curie constant (C) below 250 K indicates that each trimer has a total spin S_{total}=1/2. The large intra-trimer AF interactions give the large Weiss constant at high temperatures. The inter-trimer interactions seem to be weakly AF as suggested from the small Weiss constant of -16 K derived from the low temperature data.

In the data measured in a field of 0.1 T down to 1.8 K shown in the inset of Fig. 2, a maximum appeared at 5 K

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Scope of research

Novel 3d transition-metal oxides showing exotic electrical and magnetic properties are being searched for using different synthesizing techniques like high pressure syntesis (5 GPa and 1000°C, typically) and epitaxial film growth. Recent topics are:

- *High T_c superconductivity.*
- *Low-dimensional spin systems like ladders showing dramatic quantum effects.*
- *Oxides of late 3d transition metals like $SrFeO_3$ with strong oxygen-hole character.*

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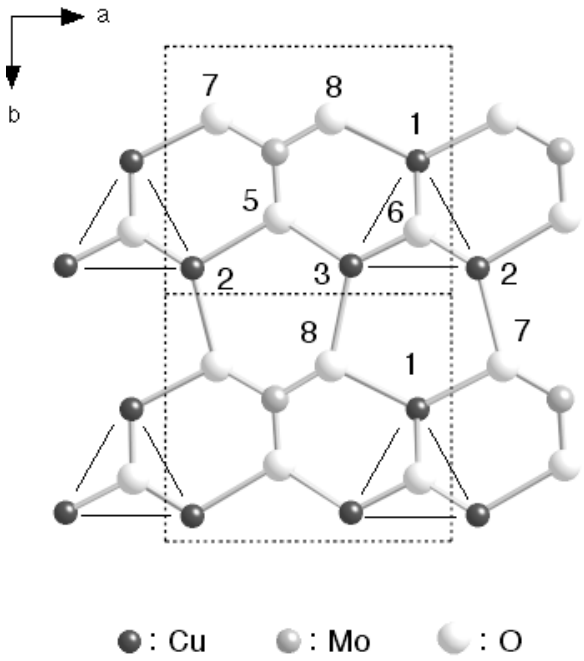

Figure 1. Cu_3MoO_4 plane of $La_4Cu_3MoO_{12}$. The numbers show the crystallographic sites. The solid line represent the triangle clusters.

and a kink at 2.6 K followed. The existence of the kink was clearly seen as a peak in the specific heat data. As can be seen in Fig. 1 there is no spin frustration among the S_{total}=1/2 spins, so it is reasonable to assume that the anomaly results from AF order of spin trimers. The susceptibility maximum at 5 K can be attributed to short range order in the two dimensional spin system. The elastic neutron scattering study confirmed the antiferromagnetic order with an ordered moment of 0.8 μ_B per trimer.

We propose the following picture for the present compound. Above 400 K, the susceptibility could be explained assuming S=1/2 spin localized on each Cu ion. The large AF interactions within the triangles led to a large Weiss temperature of -558 K. With decreasing the

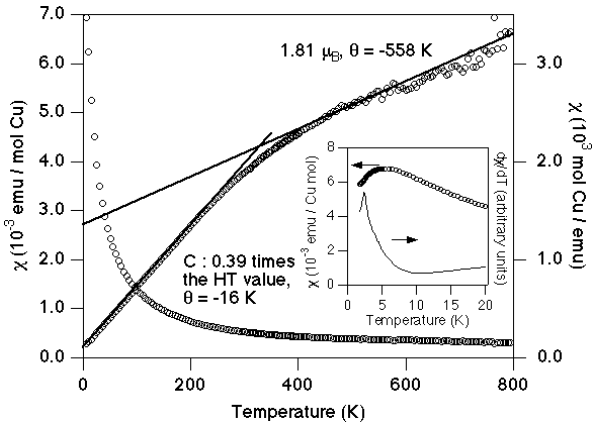

Figure 2. Temperature dependence of magnetic susceptibility of $La_4Cu_3MoO_{12}$ below 800 K. The solid lines correspond the fit to the Curie-Weiss law. The inset shows the data taken at 0.1 T.

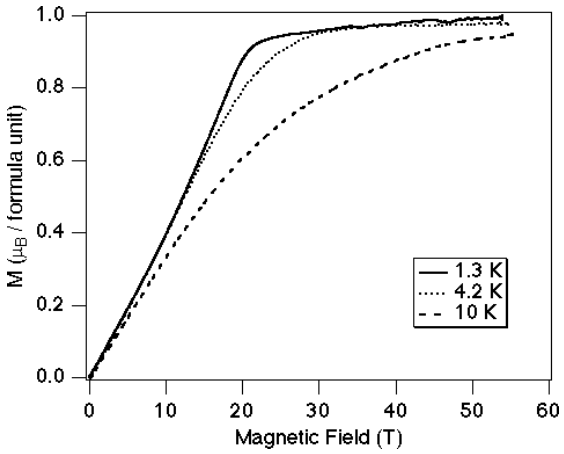

Figure 3. Magnetization curve of $La_4Cu_3MoO_{12}$ measured in pulsed magnetic field at 1.3, 4.2 and 10 K.

temperature, the Curie constant decreased to about 1/3 of the high-temperature value because only the ground state with S_{total}=1/2 per cluster was populated. Since the inter-triangle interactions are weak, the Weiss temperature is as small as -16 K. The S_{total}=1/2 spins localized on the trimers order antiferromagnetically at 2.6 K. If inter-triangle interactions are weak, it should be possible to align the ordered spins by applying magnetic field (spin flip). The results of the magnetization measurements at 1.3, 4.2 and 10 K are shown in Fig. 3. At 1.3 K, the data below 20 T were concave reflecting the AF ordering, whereas above 20 T the magnetization tended to saturate at 1 μ_B / formula unit, *i. e.*, 1 μ_B per trimer. This confirms that the system orders antiferromagnetically keeping the nature of the ground state with S_{total}=1/2. The full magnetization of this system should be 3 μ_B / formula unit, so the observed saturation-like behavior is actually an intermediate plateau. The excitation energy from S_{total} = 1/2 to S_{total} = 3/2 state is 3/2 J for an equilateral triangle. Applying J = 813 K estimated from the fitting of the susceptibility data, it is expected that another spin flip will be observed at 1500 T. Actually, inelastic neutron scattering data showed a well defined excitation at ΔE=133 meV (1542 K) which can be associated with an intratrimer doublet-quartet (S_{total}=1/2 to S_{total}=3/2) transition.

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